

CHROM. 4630

DETERMINATION OF POLYNUCLEAR HYDROCARBONS IN ATMOSPHERIC DUST BY A COMBINATION OF THIN-LAYER AND GAS CHROMATOGRAPHY

D. BROCCO, V. CANTUTI AND G. P. CARTONI

Laboratorio sull'Inquinamento Atmosferico, C.N.R. Istituto di Chimica Analitica, Università di Roma, Rome (Italy)

SUMMARY

Polynuclear hydrocarbons contained in the atmospheric dust are analyzed by a combination of thin-layer and gas chromatography. The dust as such, or a cyclohexane extract, is applied on a silica gel plate and developed with cyclohexane-benzene (1:1.5).

In this way polynuclear hydrocarbons are separated from other classes of components such as paraffins, heterocyclics, etc. The part containing polynuclear hydrocarbon is extracted again and examined by gas chromatography on a glass capillary column.

INTRODUCTION

The analysis of polynuclear hydrocarbons contained in atmospheric dust is usually carried out by the following methods:

(1) Separation of the compounds by column chromatography and determination of each constituent in the eluted fractions by spectrophotometry or fluorimetry.

(2) Separation and quantitative determination by gas chromatography after solvent extraction.

(3) Separation by thin-layer chromatography and approximate determination of the compounds on the spots or elution of the substances and determination by spectrophotometry or fluorimetry.

Detailed examination of each of these methods showed that there are many difficulties and that none are satisfactory for use in routine analysis at various air pollution control stations.

In all these methods the sample has to be extracted for many hours and large volumes of solvents have to be used. Consequently for the subsequent steps it is necessary to concentrate the large volumes of solution with the risk of losing or destroying some of the compounds.

In the first method the separation by column chromatography takes a long

time; many fractions need to be collected and many measurements with the spectrophotometer or fluorimeter are required to obtain the complete analysis.

In the second method, although the gas chromatographic procedure is more sensitive and faster, there are many preliminary steps in the preparation of the sample before its injection into the gas chromatograph. A large part of the time required to complete the analysis is taken up by the Soxhlet extraction, separation of the paraffins from the polynuclear hydrocarbons by partition between two solvents (cyclohexane and nitromethane) and evaporation of a large volume of solvent to concentrate the sample to a very small volume.

The third method, using thin-layer chromatography alone, is very simple for the separation of the compounds. However, this separation is not complete; there are too many compounds in the dust to be separated by a single chromatogram and the quantitative determination is very approximate.

As a result of these difficulties we are now studying a procedure which is based on gas chromatography for the separation of the polynuclear hydrocarbons where we try to eliminate all the preliminary steps by using thin-layer chromatography for the preparation of the sample to be injected in the gas chromatograph. Gas chromatography carried out with glass capillary columns and temperature programming give a satisfactory separation for many of the most interesting compounds¹. The retention index system is used for the identification of the peaks and by means of an internal standard it is possible to obtain the relative quantities.

The thin-layer chromatography was only used as a preliminary step to separate the various classes of compounds. Silica gel and alumina plates were tried. With the former the separation achieved was better. Solvents of different polarity were used: cyclohexane, hexane, benzene, ether. With cyclohexane or hexane alone the polynuclear hydrocarbons have low R_F values and are not resolved from the other constituents of atmospheric dust. With the other solvents the R_F values were too high. By

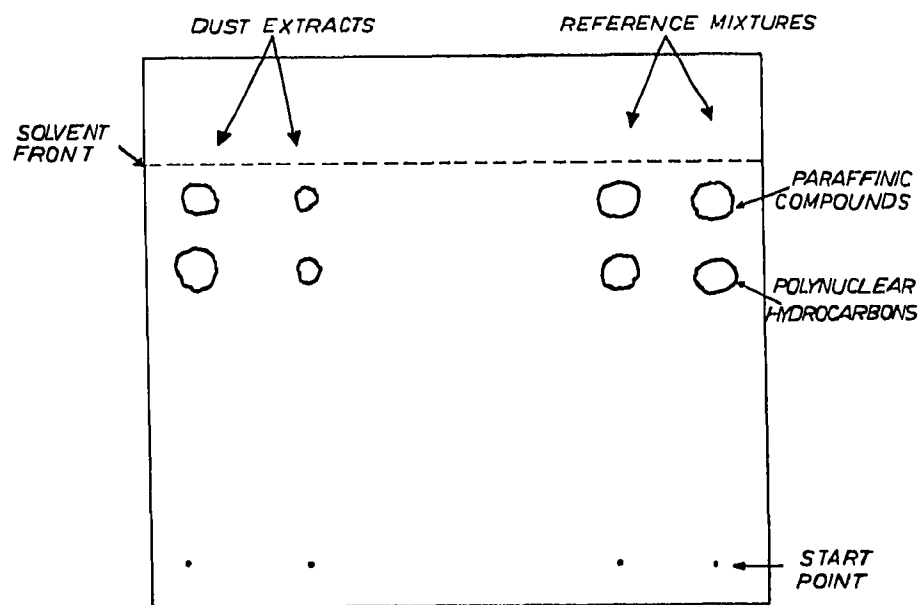


Fig. 1. Separation of paraffinic compounds from polynuclear compounds by thin-layer chromatography. Silica gel plate 500 μ thick; solvent, benzene-cyclohexane (1.5.1)

using a mixture of cyclohexane-benzene in the ratio 1:1.5, it was possible to obtain R_F values in the range 0.65-0.75 for all the polynuclear compounds tested. At the same time the paraffins are all found together very near the front, while more polar compounds, such as oxygen or nitrogen heterocyclics, are very strongly retained near the starting point (Fig. 1).

In Table I are reported the R_F values of some polynuclear hydrocarbons and paraffins on Silica Gel G and alumina plates developed with different solvents.

TABLE I

 R_F VALUES OF SOME TYPICAL POLYCYCLIC AND PARAFFINIC HYDROCARBONS

Compounds	R_F values on silica gel				R_F values on Alumina G			
	Cyclohexane	Hexane	Benzene	Ether	Cyclohexane	Hexane	Benzene	Ether
<i>Polycyclic</i>								
Anthracene	0.31	0.25	0.74	0.95	0.55	0.42	0.95	1.00
3,4-Benzofluoranthene	0.17	0.12	0.64	0.95	0.30	0.078	0.71	1.00
1,2-Benzopyrene	0.20	0.13	0.75	0.95	—	—	0.89	1.00
3,4-Benzopyrene	0.20	—	—	0.95	0.38	0.078	0.86	1.00
Fluoranthene	0.23	0.19	0.70	—	0.46	0.34	0.85	1.00
3-Methylpyrene	0.26	0.20	0.66	0.93	0.49	0.27	0.93	1.00
Pyrene	0.27	0.18	0.67	0.95	0.51	0.30	0.91	1.00
<i>Paraffins</i>								
C ₁₈	0.72	0.72	0.79	1.00	0.98	0.94	0.94	1.00
C ₂₀	0.73	0.72	0.79	1.00	0.98	0.94	0.94	1.00
C ₂₂	0.72	0.72	0.79	1.00	—	—	—	—
C ₂₄	0.72	0.72	0.79	1.00	0.86	0.94	1.00	1.00
C ₂₆	0.72	0.72	0.79	1.00	0.98	0.94	0.94	1.00

PROCEDURE

Dust is collected from the air by means of a high volume air pump (Staplex) for the time necessary for about 100-200 mg of dust to be collected in the filter. The filter with the dust is extracted in a Soxhlet with 100 ml of cyclohexane for about 8-10 h. The cyclohexane is concentrated to a small volume (about 0.1 ml) and transferred onto a thin-layer plate. A standard mixture of polynuclear hydrocarbons is run alongside the cyclohexane extract which is applied repeatedly as a 10-cm-long line till the whole extract is on the plate. The plate is then developed with the solvent mixture (cyclohexane-benzene, 1:1.5), dried and observed under a UV lamp. The fluorescent part, containing the polynuclear hydrocarbons with an R_F range 0.65-0.75 is separated and scraped from the plate into a small test tube. The compounds are then extracted 2-3 times with small portions of ether, the ether fractions are collected in a test tube with a conical end and the solvent is evaporated to a few microlitres. To obtain quantitative results it is necessary to add an internal standard to this solution. 1,3,5-Triphenylbenzene was used for these determinations.

The gas chromatographic separations are carried out with a Carlo Erba Fracto-

TABLE II

RECOVERIES OF SOME POLYCYCLIC HYDROCARBONS

<i>Compounds</i>	<i>Added</i> (μg)	<i>Found</i> (μg)
Phenanthrene	9.4	8.4
Fluoranthene	2.9	2.4
3-Methylpyrene	2.8	2.5
3,4-Benzofluoranthene	2.6	2.0
3,4-Benzpyrene	2.2	1.9

vap Model C. The column used is a glass capillary 30 m long with an efficiency of about 50,000 theoretical plates.

The silicone rubber SE-52 which is slightly polar and has a good thermal stability, is used as liquid phase.

In Table II are reported the quantitative results obtained for some polynuclear hydrocarbons analyzed with the procedure reported above.

TABLE III

QUANTITATIVE DETERMINATION OF POLYNUCLEAR HYDROCARBONS IN ATMOSPHERIC DUST ($\mu\text{g/g}$)

<i>Compounds</i>	<i>Cyclohexane</i>	<i>Nitromethane</i>	<i>Dust</i>
Phenanthrene	3.35	4.0	7.25
Fluoranthene	5.5	5.5	8.75
Pyrene	13.0	7.15	11.25
1,12-Benzfluoranthene	21.5	20.5	23.0
3,4-Benzfluoranthene			
1,2-Benzpyrene	21.5	10.0	21.0
3,4-Benzpyrene			

CONCLUSIONS

In Table III the values obtained from the determinations of some polynuclear hydrocarbons identified in atmospheric dust are compared. The analysis has been carried out on the same dust sample using three different methods: applying the cyclohexane solution from the Soxhlet extraction or the nitromethane fraction prepared according to the procedure described in previous papers to the plates¹⁻³ and directly applying a small amount (50-100 mg) of the atmospheric dust on a thin line at the starting point on the plate.

This system which combines thin-layer and gas chromatography takes advantage of the best properties of both these techniques: the fast and simple procedure of thin-layer chromatography to isolate and purify the sample and the high sensitivity and resolution of gas chromatography to separate and evaluate each single constituent.

REFERENCES

- 1 A. LIBERTI, G. P. CARTONI AND D. CANTUTI, *J. Chromatog.*, 15 (1964) 15.
- 2 V. CANTUTI, G. P. CARIONI, A. LIBERTI AND A. TORRI, *J. Chromatog.*, 17 (1965) 60.
- 3 G. ALBERINI, V. CATUTI AND G. P. CARTONI, in A. B. LITTLEWOOD (Editor), *Gas Chromatography 1964*, Institute of Petroleum, London, 1966, p. 256.